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The Repetitive Diels-Alder Reaction: A new Approach to [60]Fullerene Main-Chain Polymers

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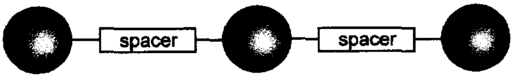
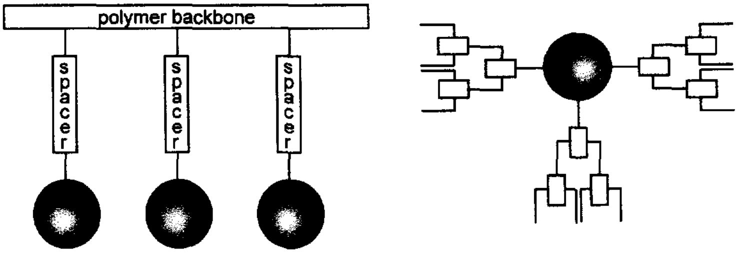
Abstract: Main-chain polymers with incorporated [60]fullerene units are accessible by reaction of buckminsterfullerene with functionalized bis-*o*-quinodimethanes. Cross linking can be effectively suppressed by carefully directed admixing of a mono-*o*-quinodimethane. The polymer **11(n)** of high molecular weight and excellent solubility, consisting of 80 [60]fullerene units on the average, is affordable. This polymer can be processed to thin amorphous films of high quality by spin coating.

INTRODUCTION

Many applications of the promising electronic [1], optical [2] and catalytical [3] properties of [60]fullerene, e.g., in surface coatings, require its immobilization. In principle, this can be accomplished in two ways: either by admixing of [60]fullerene to a polymer (noncovalent immobilization) or by covalent incorporation of [60]fullerene into polymers. The latter may be advantageous in cases where a) the fullerene unit should be more strongly bound, b) heterogeneous mixtures of [60]fullerene and the polymer tend to undergo phase separation, or c) a precise tuning of the material properties is desirable. According to the type of covalent connection of the fullerene units in the polymer, a distinction can be made between main-chain polymers, side-chain polymers and dendrimers (scheme 1).



main-chain polymer



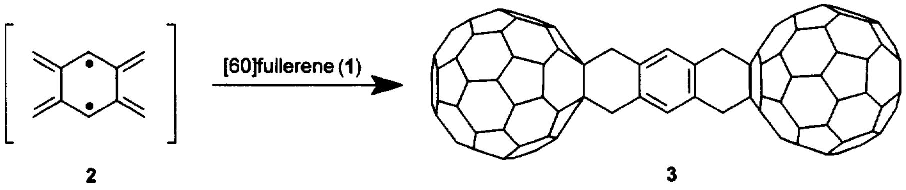
side-chain polymer *dendrimer*

Scheme 1: Structures of various [60]fullerene polymers

Whereas the synthesis of [60]fullerene side-chain polymers [4] and dendrimers [5] has already been published, polymers with [60]fullerene units in the main-chain are only scarcely known [6]. In this publication we will present a simple approach to soluble, and thereby processible, [60]fullerene main-chain polymers.

RESULTS AND DISCUSSION

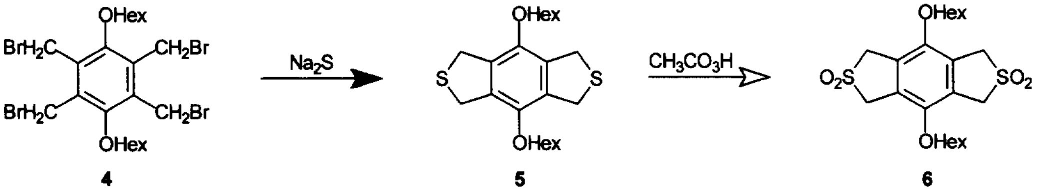
[60]Fullerene (**1**) is an electron poor alkene and hence reacts readily with numerous dienes in a [4+2] cycloaddition reaction (Diels-Alder reaction) [7]. In particular, cycloaddition reactions with *o*-quinodimethanes have proven to be very useful because, unlike most other methods, they yield very stable adducts [7a,b,e,f]. In principle, the construction of main-chain polymers is possible by repetitive cycloaddition of [60]fullerene, which acts as a multi-functional dienophile, with the bis-*o*-quinodimethane **2** (scheme 2).



Scheme 2: Synthesis of the "dumb-bell" compound **3**

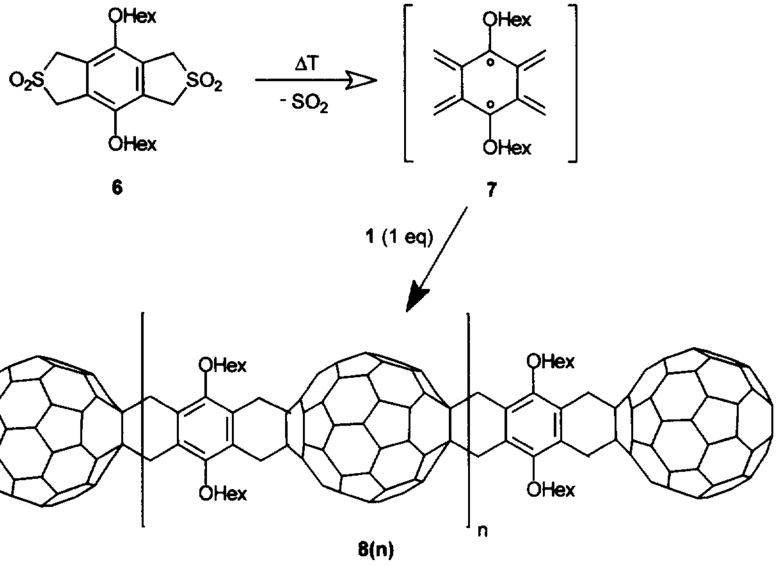
We were able to show that the "dumb-bell" compound **3** is formed [7a]. Nevertheless, the derivation of processible main-chain polymers containing [60]fullerene using this approach was thwarted by the poor solubility of **3** and the formation of higher molecular weight products.

Thus, it was necessary to improve the solubility of the reaction products by the introduction of flexible, hence solubilizing, substituents. Furthermore, another approach to bis-*o*-quinodimethanes was required because the reactions with tetramethylbenzene-derivatives require very long reaction times (several days) on the one hand and, on the other, the halogens formed can lead to undesirable by-products by direct addition to the [60]fullerene core. For these reasons, the bis-hexyloxy-substituted bis-sulfone **6** was synthesized according to the reaction sequence shown in scheme 3a.



Scheme 3a: Reaction sequence for the preparation of **6**

This compound was treated with an equimolar amount of **1** in refluxing 1,2,4-trichlorobenzene. After 20 h reaction a soluble mixture of the oligomer **8(n)** was formed (scheme 3b).



Scheme 3b: Reaction sequence for the preparation of **8(n)**

According to matrix assisted laser desorption ionisation - time of flight mass spectrometry (MALDI-TOF MS) and analytical size exclusion chromatography (SEC) (fig.1) of **8(n)** up to seven fullerene molecules (n = 0 - 5) are linked by hexyloxy-substituted spacers.

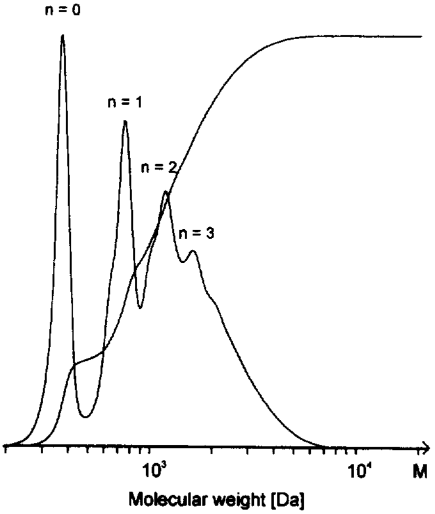


Fig. 1:

Size exclusion chromatogram of the oligomer mixture **8(n)**
column: (8 x 600 mm) x 2; stationary phase: PSS gel, 5 μm, 1000 + 10000 Å; mobile phase: chloroform, 0.7 ml min^{-1}; detection: UV (255 nm)

The oligomers appear to be terminated by mono-substituted [60]fullerene units, because no unreacted sulfone groups could be detected by mass spectrometry. This interpretation is supported by the fact that the absorption peak at about 435 nm, which is characteristic for all mono-adducts of [60]fullerene, is present for all individual oligomers and the intensity decreases with increasing molecular weight of the oligomer. This can be traced back to the fact that the ratio of the terminal mono-functionalized [60]fullerene units to the multiple-functionalized [60]fullerene units within the polymer chain (which show no absorption peak at 435 nm) also decreases with increasing molecular weight. The oligomers **8(n = 0)** and **8(n = 1)** could be isolated (fig.2) [8] by preparative liquid chromatography on polystyrene gel [9] with chloroform as mobile phase.

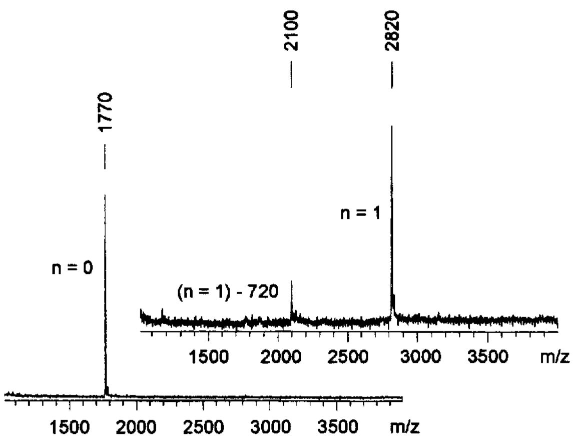
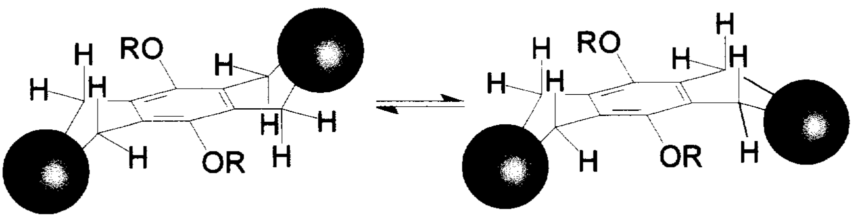


Fig. 2:

MALDI-TOF mass spectra of the oligomers **8(n = 0)** and **8(n = 1)** (matrix: 9-nitroanthracene)

The "dumb-bell" compound **8(n = 0)** is soluble in halogenated benzenes, but possesses only moderate solubility in chloroform.

Oligomer **8(n = 0)** exists as a single regioisomer so that it was possible to characterize it by ^1H NMR spectroscopy. The ^1H NMR spectrum shows that **8(n = 0)** can exist either in the cis- or in the trans-conformation (scheme 4).



Scheme 4: cis- and trans-conformers of the bis-hexyloxy-substituted "dumb-bell" compound **8(n = 0)**

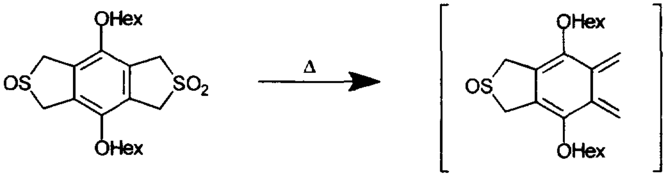
The two AB-systems for the benzylic protons with a ratio of 1 : 1.5 can be observed at room temperature. Above 30°C the change in conformation leads to line broadening and, above about 100°C (500 MHz), the signals coalesce. Theoretically, eight regioisomeric structures are possible for the tris-fullerene **8(n = 1)** and all bis-adducts of [60]fullerene [10]. Therefore, **8(n = 1)** elutes in SEC as a broadened peak with a shoulder, but the resolution is not high enough to enable separation of the regioisomers without considerable effort. The MALDI-TOF mass spectrum of the regioisomeric mixture of **8(n = 1)** shows the molecular ion peak at m/z = 2820 and minor signals of fragmentation products (fig. 2). Using MALDI-TOF mass spectrometry it was also possible to identify the "higher" oligomers **8(n = 2)** to **8(n = 5)**. Therefore, this kind of mass spectrometry seems to be the method of choice for the identification of stable fullerene derivatives of high molecular weight.

Comparison of the solubility of the various oligomers reveals noteworthy differences. The oligomeric mixture is very soluble in chloroform and can therefore be separated by chromatography on polystyrene gel. After separation the "dumb-bell" compound **8(n = 0)** precipitated. Subsequently, it could be only redissolved in halogenated aromatics (e.g. 1,2-dichlorobenzene). Without doubt, this poor solubility can be attributed to a weak intermolecular interaction between the electron-rich bis-hexyloxy-substituted bridge in **8(n = 0)** and the electron-poor [60]fullerene unit of a second molecule **8(n = 0)**. In contrast, the "higher" oligomers remain dissolved for an unlimited period. Presumably, this can be traced back to the increasing "irregularity" of the molecule, which is determined by the increasing number of regioisomeric structures.

In order to increase the molecular weight, the oligomeric mixture **8(n)** was further treated with an additional equivalent of the bis-sulfone **6**, which gave only an insoluble product. This result is by no means surprising, because [60]fullerene is a multifunctional reactant and, therefore, multiple additions ultimately lead to cross linking.

In additions of *o*-quinodimethanes to [60]fullerene the tris-adducts are easily formed, whereas the tetra-adducts are not. Therefore, we added the mono-sulfone **9** to the bis-diene precursor **6**, which should effectively suppress cross linking and enable preparation of soluble polymers.

The mono-sulfone **9** is especially well suited for this purpose, because it is easily accessible by oxidation of **5** with peroxo acetic acid under milder conditions (compared with those required for the preparation of **6**). Compound **9** only undergoes elimination to the mono-*o*-quinodimethane **10** (scheme 5) which also adds to the fullerene units in the polymer.

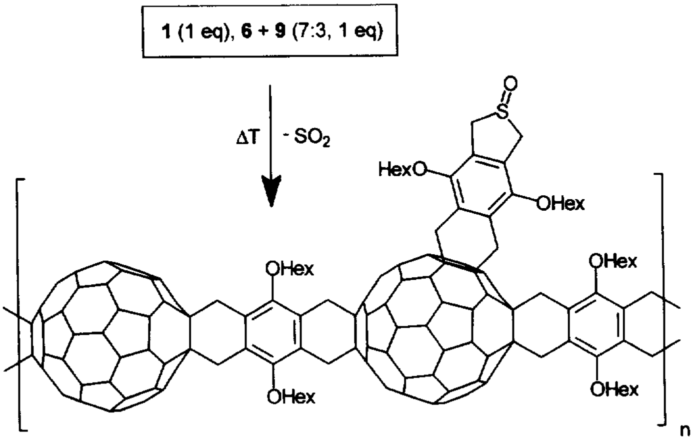


9 **10**

Scheme 5: Synthesis of *o*-quinodimethane **10**

Conditional on the triple functionalization of some polymer units with **10**, a further addition, which is necessary for cross linking to occur, becomes less probable. In addition, the mono-*o*-quinodimethane acts as a solubilizing group. Reaction of [60]fullerene with one equivalent of a mixture of **6** and **9** (7:3) (same conditions as for the reaction of **1** with **6**) also yields a soluble mixture of oligomers **11** with a decamer

(n_{max} = 8) as the highest molecular weight species, according to MALDI-TOF MS (scheme 6). The molecular weight distribution is very similar to that of the previously described oligomer mixture **8(n)**, but the MALDI-TOF MS of the reaction product shows additional peaks for oligomers modified with mono-*o*-quinodimethane **10**.



11(n)

Scheme 6: Synthesis of the polymer **11(n)**

Subsequently, the molecular weight was increased by further reaction with one additional equivalent of the **6**/**9**-mixture (7:3). The resulting product is completely soluble and the polymer has M_w 17000 and M_n 3600 (determined by SEC). These values are based on calibration with a polystyrene standard. Comparison of these values with those determined by MALDI-TOF MS reveals that the molecular weights must be multiplied by a factor of at least 2 [11]. Consequently, the "true" molecular weights are at least 34000 (M_w) and 7200 (M_n). The polymers are completely soluble in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene but only partly soluble in toluene or chloroform. Therefore, a high molecular weight fraction with M_w 80000, M_n 38000 and $P_n \approx 80$ (in each case multiplied by a correction factor of 2) could be isolated by separation of the lower molecular weight material by extraction with chloroform. The high molecular weight fraction makes up about one third of the complete product mixture. On account of the excellent solubility of **11(n)** it was possible to prepare thin, amorphous films by spin coating. The investigation of a 2 nm thick film by ellipsometry shows a refractive index n_D of 1.75.

CONCLUSION

We have demonstrated that bis-*o*-quinodimethanes are especially well suited for the preparation of main-chain polymers with incorporated [60]fullerene units. Nevertheless, some prerequisites must be fulfilled to afford soluble polymers: Flexible, solubilizing functional groups should be attached to the bis-*o*-quinodimethanes and cross linking must be suppressed. The latter was accomplished by addition of a mono-*o*-quinodimethane to the reaction mixture. The mono-*o*-quinodimethane also adds to the [60]fullerene units in the polymer.

Thus, cross linking on these units, which would require the formation of tetra-substituted building blocks, is effectively suppressed. In this manner we could synthesize a soluble polymer with M_w 80000 and M_n 34000. We are currently investigating the application potential of this polymer.

EXPERIMENTAL

[60]Fullerene **1** (360 mg, 0.5 mmol) and 1,3,5,7-tetrahydro[1,2-c:4,5-c′]dithiophene-2,2,6,6-tetraoxide **6** (229 mg, 0.5 mmol) were refluxed in 100 ml of 1,2,4-trichlorobenzene for 20 h. After cooling, 50 ml of the red-brown solution was poured into 100 ml of methanol. The precipitate was filtered off, washed three times with methanol, dissolved in chloroform and subsequently separated by chromatography on polystyrene gel.

The remaining 50 ml of the solution was mixed with **6** (114 mg, 0.25 mmol = 1 eq) and refluxed for another 20 h, leading to a precipitate that was insoluble in common organic solvents, and which, therefore, could not be characterized.

8(n = 0): MS (MALDI-TOF; 9-nitroanthracene as matrix): m/z = 1770 ($[M]^-$, 100 %); ^{1}H NMR (500 MHz; 1,2-dichlorobenzene-d_4; 0°C, two conformers in a ratio of 1 : 1.5): Conformer A: δ = 0.85 (m, 6H, CH_3), 1.20 - 1.60 (m, 12H, CH_2), 2.03 (m, 4H, CH_2), 4.24 (m, 4H, OCH_2), 4.75 (d, 4H, *J* = 13 Hz), 5.25 ppm (d, 4H, *J* = 13 Hz); Conformer B: δ = 0.85 (m, 6H, CH_3), 1.20 - 1.60 (m, 12H, CH_2), 2.03 (m, 4H, CH_2), 4.28 (m, 4H, OCH_2), 4.78 (d, 4H, *J* = 13 Hz), 5.16 ppm (d, 4H, *J* = 13 Hz); UV/Vis (chloroform): similar to that of [60]fullerene, but with an additional small absorption peak at about 435 nm.

8(n = 1): MS (MALDI-TOF; 9-nitroanthracene as matrix): m/z = 2820 ($[M]^-$, 100 %), 2100 ($[M-720]^-$, 25 %); UV/Vis (chloroform): similar to that of [60]fullerene, but with an additional small absorption peak at about 435 nm.

8(n = 2): MS (MALDI-TOF; 9-nitroanthracene as matrix): m/z = 3870 ($[M]^-$, 100 %), 3150 ($[M-720]^-$, 15 %), 2820 ($[M]^-$ of **7(n = 1)**, 10 %); UV/Vis (chloroform): similar to that of [60]fullerene, but with an additional small absorption peak at about 435 nm.

11(n): **1** (360 mg, 0.5 mmol) and a mixture of 1,3,5,7-tetrahydro[1,2-c:4,5-c']dithiophene-2,2,6,6-tetraoxide **6** and 1,3,5,7-tetrahydro[1,2-c:4,5-c']dithiophene-2,2,6-trioxide **9** (225 mg, 0.5 mmol) (7:3) in 100 ml 1,2,4-trichlorobenzene were refluxed for 20 h. After cooling, 50 ml of the red-brown solution was poured into 100 ml methanol. The precipitate was filtered off, washed three times with methanol, dissolved in chloroform and separated by chromatography on polystyrene gel.

The remaining 50 ml of the solution was split into two portions and further treated with a) 0.5 eq. and b) 1 eq. of the sulfone mixture **6** / **9** (7:3) for 20 h. After work-up, described previously, both samples were analyzed using analytical SEC.

ACKNOWLEDGEMENT

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8. The structures of **8(n)** and **11(n)** in scheme 3a/b and 6 are idealised and represent a mixture of regioisomers.
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11. Due to interaction of the samples with the stationary phase (polystyrene gel) all [60]fullerene-containing compounds show a retention volume that is too large. Consequently, the molecular weights determined are too small. Therefore, the determination of correct molecular weights requires an internal calibration. This calibration was performed using MALDI-TOF mass spectrometry of the oligomers **8(n)**. The correction factor applied is 2 - 4.

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